Evaluating the Effect of Conformal Coatings in Reducing the Rate of Conductive Anodic Filament Formation

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ABSTRACT

Conductive anodic filament (CAF) formation is a failure mode in printed wiring boards (PWB) which occurs when the circuit is operated under a high voltage gradient. Humidity also plays a factor since the boards must be stored, or operated in a humid environment. This failure mode is enhanced by certain water soluble fluxes or hot air solder leveling (HASL) fluids. The objective of this research was to examine the effect of three different conformal coatings in reducing the incidence of CAF associated with a variety of water-soluble flux formulations. To achieve this, a series of fluxes were evaluated for their propensity to enhance CAF. Several of these were chosen for further examination with acrylic, silicone and parylene C conformal coatings. Of the three conformal coatings tested only parylene C was effective in preventing CAF and dendrite formation in all cases. Silicone coatings showed bubbles present on some of the samples aged at 85°C for the 28-day test. Localized debonding occurred on some of the acrylic and the parylene C boards. Also, some boards exhibited localized debonding of epoxy/glass after during aging of the coating, suggested chemical interactions with flux residues creating mechanical stresses.

One set of boards was subjected to higher processing temperatures similar to those that would be associated with lead-free soldering. When compared to boards processed with the same fluxes using the lower processing temperatures, the high temperature boards showed significant increase in CAF formation.

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I. BACKGROUND

There is a need for a more fundamental understanding of the interaction of processing chemicals such as fusing fluids, soldering fluxes and cleaning agents with printed wiring board substrates. This need is driven by two factors (1) the increased density of today's electronic products creates voltage gradients which are high enough to enhance degradation modes which are not important for less dense circuitry, and (2) the elimination of chlorofluorocarbons (CFCs) and other ozone depleting cleaning agents due to their destructive effect on the stratospheric ozone layer has lead to a proliferation of new soldering fluxes and cleaning agents [1] whose interactions with the printed wiring board (PWB) are not well characterized.

Twenty years ago, researchers at Bell Laboratories [2] identified a failure mechanism, which occurred on PWB when they were placed at high humidity under a high voltage (200V to 500V with spacing of 0.010" for surface patterns and 0.100" for hole-to-hole patterns). This failure mechanism was termed conductive anodic filament (CAF). Unlike surface dendrite formation where the metal ions go into solution at the anode and form metallic dendrites emanating from the cathode, CAF involves the formation of a conductive metal salt which grows from the anode, subsurface along the glass/epoxy interface of the FR-4 substrate (Figure 1).

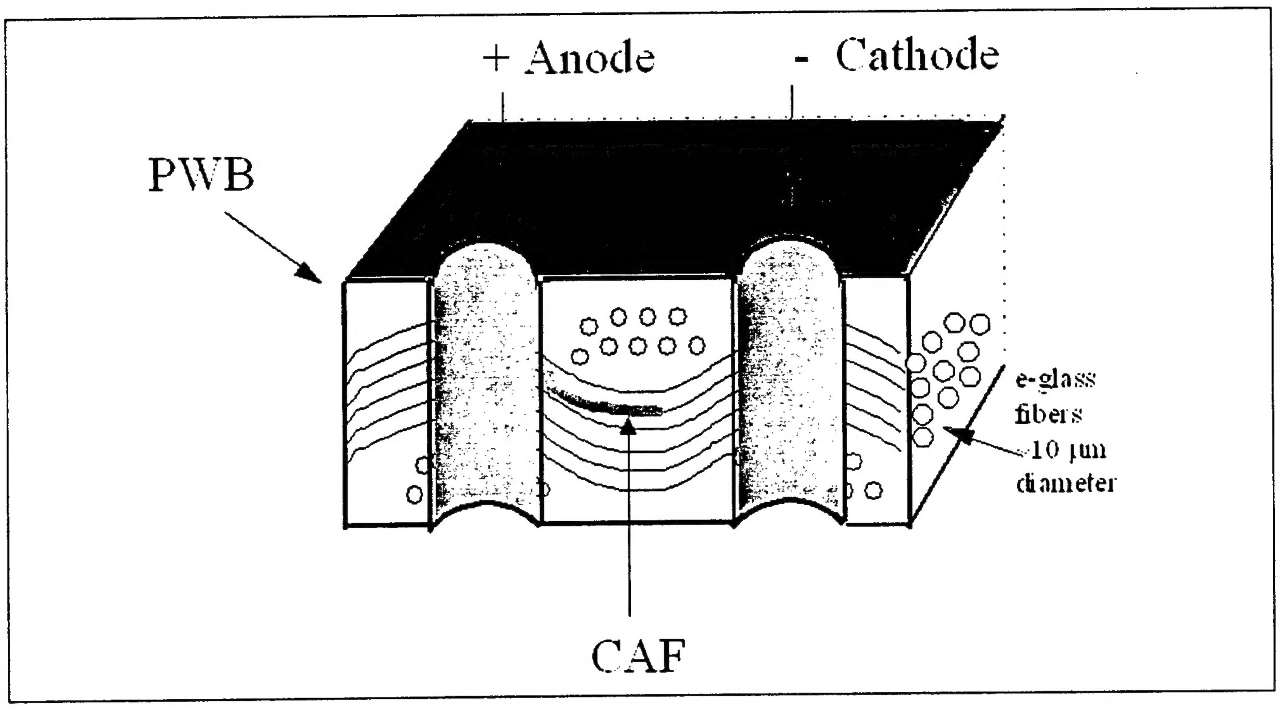

Figure 1. Conductive anodic filament (CAF) consists of a copper salt growing subsurface along the epoxy-glass interface.

Although this failure mode was identified under severe stress conditions in the 1970's, it did not create field failures until circuit densities increased in the early 90's. Recent work in our laboratory [3] has indicated that this failure mode was responsible for a catastrophic failure

identified in field returns. The failed multilayer board contained a copper-bromide containing filament which connected a + 20 V power plane with a via hole between layers 6 and 7 of a 14 layer PWB. With a nominal spacing of 0.005 and a 40 V difference in potential, this created a voltage gradient of 8 V/0.001 . This failure was correlated with the presence of ionic contamination from the soldering flux, which had diffused into the boards' inner layers during the reflow soldering process. Further work in our laboratory indicated that certain polyglycols from water-soluble fluxes (or water soluble fusing fluids) could also reduce the voltage gradient required for CAF formation to be activated.

Most military electronics hardware is stored for a period of time in warehouses where neither temperature nor humidity is controlled. When this occurs, the cumulative effect of moisture absorption (the rate limiting step defined above) is an area of concern. If the humidity of storage is high, and the circuitry is dense, then the potential for CAF failure due to circuit design and processing chemicals is real. Additionally, as circuitry becomes more complex and dense, the voltage gradient associated with the use of the electronic hardware may be sufficiently high to cause failures.

Zado [4] first identified the effect of non-ionic water-soluble flux residues in 1979. He evaluated the effect of the of the individual constituents – solvent, vehicle and activators – on surface insulation resistance (SIR) and showed that polyethylene glycol (PEG) and its octyl and nonyl derivatives which are non-ionic flux constituents cause significant degradation in insulation resistance values. He associated this degradation with the dissolution of PEG into the epoxy-glass substrate during the soldering process when the board is above its glass transition temperature (T_g). He later showed that polypropylene glycol (PPG) provides improved SIR characteristics.[5]

In 1981 Brous [6] expanded on Zado's work and reported SIR data for boards treated with a variety of water-soluble flux vehicles including glycols, polyglycols, polyglycol surfactants, glycol ethers and polyols. He found a wide variation of SIR results among the materials studied. He concluded that the actual SIR readings will depend upon several factors which include (1) the degree of polymer absorption into the substrate, (2) the effectiveness of the cleaning process, (3) the hygroscopic character of the absorbed material, (4) the volatility of the chemical, (5) the temperature and humidity of the storage conditions and (6) the presence or absence of ionic contamination from the flux.

Brous later [7]evaluated the ability of various solvents to extract the non-ionic water soluble flux residues. Boards processed with a commercial water-soluble flux and water cleaned were then oven-baked at 130°C for 24 hours. These showed almost a 40x increase in SIR readings. Other flux-processed boards soaked in acetonitrile for 24 hours had SIR levels 480x that of the processed boards. Since many SIR test boards have been through a solder-plate and reflow process using water-soluble fluxing agents, Brous incorporated an acetonitrile soak into his sample preparation procedures.

In 1997 Jachim [8] was the first to implicate polyglycol-containing fluxes with CAF. Later, Ready[9] evaluated a number of water-soluble fluxes with various polyglycols vehicles using epoxy/glass boards. He noted that some of these fluxes showed significant enhancement of CAF and he showed that the filaments are sometimes copper-chloride containing and at other times copper-bromide containing.

Studies of CAF usually involve the use of test boards containing interdigitated comb patterns such as the IPC-B-24 test coupon (Figure 2). The comb patterns are biased and placed in a temperature humidity chamber for a period of time under accelerating test conditions.

Periodically the surface insulation resistance (SIR) is measured. Temperature, humidity, voltage gradient and contamination affect this reading. The IPC industry standard uses 50V bias and 85°C/85% RH for the accelerating conditions and 100V test voltage for SIR measurements in their 7-day test. Using the IPC test coupon, a minimum value of 1E08 Ω is required at day-4 and day-7 measurements. Low SIR readings can indicate potential problems due to electrochemical migration (ECM). ECM may appear in the form of surface dendrites or of subsurface CAF.

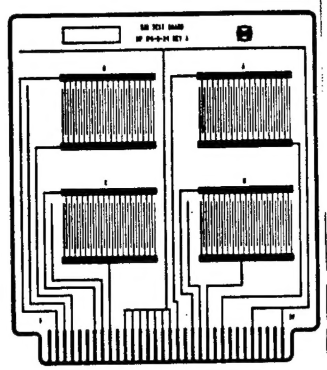

Figure 2. IPC-B-24 test coupon containing four interdigitated comb patterns.

Research Objective: The objective of this research was to examine the effect of three different conformal coatings in reducing the incidence of CAF associated with a variety of water-soluble flux formulations.

I. APPROACH

In Part I of the study SIR test boards were processed with a series of water soluble fluxes then aged at accelerating conditions of 85°C / 85% RH and 100V bias for 28 days. SIR electrical data were plotted for the various fluxes and optical microscopy was used to detect the presence of either surface dendrites or subsurface CAF. Using these results, the five formulations, which showed the worst incidents of CAF, were chosen for Part II. Water-soluble flux processed boards were conformally coated with one of three materials: acrylic, silicone or parylene C coatings. SIR testing was again performed and electrical and optical data analyzed.

II. RESULTS

A. Part I. Choice of Fluxes which Enhance CAF

There were a number of fluxes tested in this study. Table I provides the details. When HCl or HBr are indicated, they were present as 2 w% halide. In some cases monoethanol amine (MEA) was added to evaluate the effect if the amine-salt. The polyglycol or polyglycol derivative is present at 20 w% and the remaining solvent is isopropanol (IPA).

The SIR and optical evaluation of these fluxes revealed the following results for Part I.

1. CAF enhancement based on the polyglycol or polyglycol derivative follows the following decreasing order: OPE > LAP > PEPG18 > PEPG12 > GLY > PPG.

2. Analyses of the summary data show that PEG exhibits the greatest enhancement of CAF when halide activators were absent. However, when halide activators were present, no CAF or discrete dendrites were observed.
3. For the other polyglycols or polyglycol derivatives, the effect of added halide and/or MEA varied among the formulations. In some cases, chloride enhanced CAF, in others bromide or amine halide provided the greatest number of CAF.
4. The electrical SIR for PEG in call cases was below 1E06, the limiting resistance of the measuring circuit.
5. SIR data for the other formulation were unique to the formulation under study. In some cases the values for the halide-activated formulations were higher than the un-activated formulation. In others there was no significant difference.

Table I. Flux Formulations	
Polyethylene Glycol 600 (PEG)	**Glycerine GLY**
PEG/IPA PEG/HCl/IPA PEG/HCl/MEA/IPA PEG/HBr/IPA PEG/HBr/MEA/IPA	GLY/IPA GLY/HCl/IPA GLY/HCl/MEA/IPA GLY/HBr/IPA GLY/HBr/MEA/IPA
Polypropylene Glycol 1200 (PPG)	**Octyl Phenol Ethoxylate (OPE)**
PPG/IPA PPG/HCl/IPA PPG/HCl/MEA/IPA PPG/HBr/IPA PPG/HBr/MEA/IPA	OPE/IPA OPE/HCl/IPA OPE/HCl/MEA/IPA OPE/HBr/IPA OPE/HBr/IPA OPE/HBr/MEA/IPA
Polyethylene Propylene Glycol 1800 (PEPG18)	**Modified Linear Aliphatic Polyether (LAP)**
PEPG18/IPA PEPG18/HCl/IPA PEPG18/HCl/MEA/IPA PEPG18/HBr/IPA PEPG18/HBr/MEA/IPA	LAP/IPA LAP/HCl/IPA LAP/HCl/MEA/IPA LAP/HBr/IPA LAP/HBr/MEA/IPA
Polyethylene Propylene Glycol 1200 (PEPG12)	
PEPG12/IPA PEPG12/HCl/IPA PEPG12/HCl/MEA/IPA PEPG12/HBr/IPA PEPG12/HBr/MEA/IPA	

Additional results regarding the effect of temperature on CAF enhancement were obtained in study Table II.[10] Most of the study used a maximum temperature of 201°C, which represents the temperature spike associated with wave soldering. However, one set of boards reached a T_{max} of 241°C, a temperature which might occur when using lead-free solders. While

variations occurred among the fluxes tested, in general the incidences of CAF at this higher reflow temperature are 1-2 orders of magnitude greater than at the lower reflow conditions. These results suggest that lead-free soldering has the potential to greatly increase the number of failures in the field. Further work needs to be done in this area.

Table II. Comparison of SIR levels and number of CAF associated with two different reflow temperatures.

Flux	SIR (Ω) 201°C reflow	SIR (Ω) 241°C reflow	#CAF at 201°C reflow	#CAF at 241°C reflow
Polyethylene glycol-600(PEG)	$<10^6$	$<10^6$	90	55
PEG/HCl	$<10^6$	High 10^8	None	None
PEG/HBr	$<10^6$	High 10^8	None	None
Polypropylene glycol 1200 (PPG)	$>10^{10}$	$>10^{10}$	None	455
PPG/HCl	$>10^{10}$	$>10^{10}$	None	379
PPG/HBr	$>10^{10}$	$>10^{10}$	1	423
Polyethylene propylene glycol 1800 (PEPG 18)	High 10^9	High 10^9	1	406
PEPG 18/HCl	High 10^9	High 10^9	10	135
PEPG 18/HBr	10^{10}	High 10^9	9	279
Polyethylene propylene glycol 2600 (PEPG 26)	High 10^9	High 10^9	None	91
PEPG 26/HCl	High 10^9	High 10^9	6	218
PEPG 26/HBr	10^{10}	High 10^9	None	51
Glycerine (GLY)	$>10^{10}$	High 10^9	None	56
GLY/HCl	$>10^{10}$	High 10^9	None	583
GLY/HBr	$>10^{10}$	High 10^9	3	104
Ocyl phenol ethoxylate (OPE)	Low 10^9	Low 10^9	None	83
OPE/HCl	Low 10^9	Low 10^9	14	62
OPE/HBr	$>10^{10}$	High 10^9	2	599
Linear Aliphatic Polyether (LAP)	Low 10^9	Not Tested	None	Not Tested
LAP/HCl	Low 10^9	Low 10^9	15	203
LAP/HBr	Low 10^9	Low 10^9	None	272

Based on the data obtained in Part I, the following formulations were chosen for Part II evaluation of conformal coatings: PEG/IPA, PEPG18/HCl/IPA, OPE/HBr/MEA/IPA,

LAP/HCL/IPA, LAP/HCl/MEA/IPA and LAP/HBr/MEA/IPA. The conformal coatings tested were acrylic (Humiseal 1B73), silicone (Humiseal 1C55) and parylene C. Table III summarizes the CAF observations for the various flux/conformal coatings combinations. Table IV summarizes the dendrites observed.

Of the three conformal coatings tested only parylene C was effective in preventing CAF and dendrite formation in all cases. The acrylic coating eliminated CAF for some formulations and reduced it for others while the silicone coating only prevented CAF on the PEG/IPA coupons, reduced it on others, and marginally increased it in the case of LAP/HCl/IPA. Dendrite formation actually increased for PEG/IPA with acrylic or silicone coatings compared to the control. The silicone coating also increased dendrite formation for LAP/HCl/MEA/IPA.

Table III. CAF results for various flux and conformal coating combinations.

Flux	Uncoated	Acrylic	Silicone	Parylene C
PEG/IPA	Yes (~90)	None observed	None observed	None observed
PEPG18/HCl/IPA	Yes (~21)	None observed	Yes (~4)	None observed
OPE/HBr/MEA/IPA	Yes (~62)	Yes (~40)	Yes (~16)	None observed
LAP/HCl/IPA	Yes (~15)	None observed	Yes (~20)	None observed
LAP/HCl/MEA/IPA	Yes (~31)	Yes (~25)	Yes (~10)	None observed
LAP/HBr/MEA/IPA	Yes (~27)	Yes (~14)	Yes (~9)	None observed

Table IV. Dendrite results for various flux and conformal coating combinations.

Flux	Uncoated	Acrylic	Silicone	Parylene C
PEG/IPA	None observed	Many dendrites	Moderate amount	None observed
PEPG18/HCl/IPA	Small amount	None observed	None observed	None observed
OPE/HBr/MEA/IPA	None observed	None observed	None observed	None observed
LAP/HCl/IPA	None observed	None observed	None observed	None observed
LAP/HCl/MEA/IPA	None observed	None observed	Moderate amount	None observed
LAP/HBr/MEA/IPA	None observed	None observed	None observed	None observed

Microscopic examination of silicone-coated PEG/IPA coupons revealed an unexpected and unusual observation. Crosshatched white marks (Figure 3) appeared within the PWB which, on enlargement, appear to be localized debonding at the epoxy-glass interface (Figure 4). This phenomenon was also observed in the case of acrylic-coated LAP/HCl/MEA/IPA. This debonding did not appear on the uncoated coupons. The proposed mechanism of formation would involve chemical interaction between the flux and conformal coating creating mechanical stresses sufficient to debond the glass fibers from the epoxy in localized areas of the PWB.

Figure 3. : Image showing white marks observed on silicone-coated PEG/IPA test coupons after aging. The marks appear to follow the weave of the glass fibers.

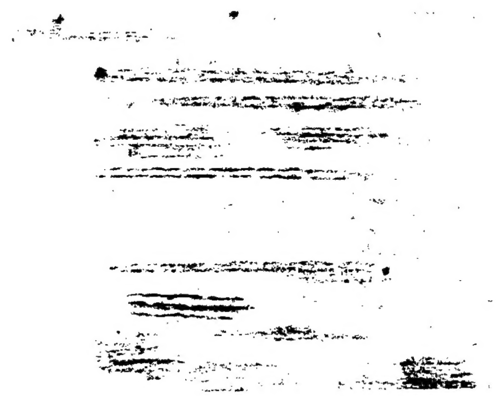

Figure 4. Enlarging these white marks shows that there is localized de-bonding at the epoxy/glass fiber interface. (This image was acquired using reflected illumination.)

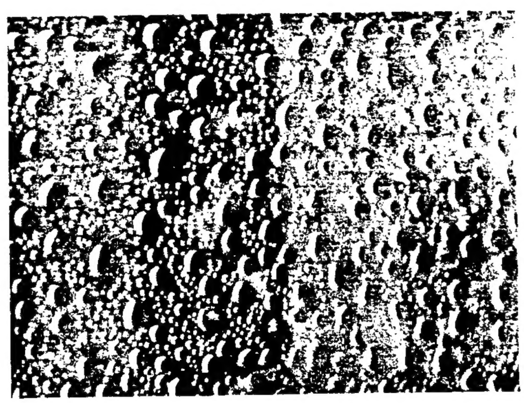

Figure 5. Image showing bubbles observed in silicone-coated coupons.

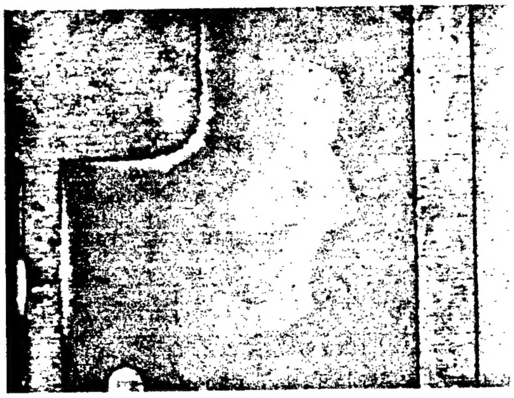

Figure 6. Image shows a blister spot at the acrylic coating/epoxy interface, on the LAP/HBr/MEA/IPA test coupon.

Bubbles were observed for all of the silicone-coated boards, but were most pronounced for those processed with PEG/IPA and the various LAP formulations. It appears that the polyglycol or polyether is diffusing out of the board and through the silicone, creating this bubbling effect at the 85°C accelerating conditions.

Localized debonding sites were observed for some of the acrylic-coated boards, namely those processed with PEG/IPA, and LAP/HBr/MEA/IPA. Large areas of localized debonding were also observed on PEG/IPA and LAP/HCl/IPA coupons coated with parylene C.

Impact/Navy Relevance

Military Specifications have always detailed the type of soldering fluxes that were allowed for use in the manufacture of military hardware. With the demise of these specifications, industry practice and specifications are applied. But even when Mil-Specs defined the allowed soldering fluxes, no regulations existed for the hot air solder leveling (HASL) fluids used in the manufacture of the printed wiring boards. Thus, there is a great deal of Navy and other DoD product in the field that has been processed with these polyglycol-containing chemicals.

The use of conformal coating on some military product is designed to prevent condensation and dendritic growth when the electronics are exposed to high humidity, condensing or corrosive environments. It is postulated that the conformal coating provides a measure of protection from CAF field failures by reducing the rate of CAF growth. Based on the results of this present study, it is clear that the amount of CAF protection will be determined by the combination of flux-formulation and conformal coating chosen. Parylene C provides the best CAF protection.

More research needs to be performed on soldering flux formulations and their relationship to CAF formation and the best flux/conformal coating options. From the present study it is clear that variation in the polyglycol chosen will determine if halide and/or amine activators enhance or reduce CAF.

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14. ABSTRACT

Conductive anodic filament (CAF) formation is a failure mode in printed wiring boards (PWB) which occurs when the circuit is operated under a high voltage gradient and is enhanced by certain water soluble fluxes or hot air solder leveling (HASL) fluids. Humidity also is a factor, and this project examined how well three different conformal coatings reduced CAF accompanying various water-soluble fluxes. A series of fluxes were evaluated for their propensity to enhance CAF. Several were examined further with acrylic, silicone and parylene C conformal coatings. Only parylene C prevented CAF and dendrite formation in all cases. Silicone coatings showed bubbles in some of the samples aged at 85°C for the 28-day test. Localized debonding occurred on some of the acrylic and the parylene C boards and at epoxy/glass interfaces after coating aging which suggests chemical interactions with flux residues create mechanical stresses. One set of boards was processed at higher temperatures similar to those associated with lead-free soldering. Compared to boards processed with the same fluxes at lower temperatures, the high temperature boards showed significant increase in CAF formation.

15. SUBJECT TERMS: conformal coating, electronics manufacturing, conductive anodic filamanent (CAF), reliability (electronics), printed wiring boards (PWBs), copper, corrosion

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